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New Multi-1,2,3-Selenadiazole Aromatic Derivatives

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Abstract: The aromatic polyketones **3a-d** are versatile compounds for the synthesis of the multi-1,2,3-selenadiazole aromatic derivatives **1a-d**. The preparation starts with the reaction between the multi-bromomethylene benzene derivatives **2a-d** and 4-hydroxy-acetophenone to give compounds **3a-d** which are transformed through the reaction with semicarbazide hydrochloride or ethyl hydrazine carboxylate into the corresponding semicarbazones derivatives **4a-d** or hydrazones **5a-d**. The reaction with selenium dioxide leads to regiospecific ring closure of semicarbazones or hydrazones to give the multi-1,2,3-selenadiazole aromatic derivatives in high yield.

Keywords: 1,2,3-Selenadiazoles; semicarbazones; aromatic derivatives

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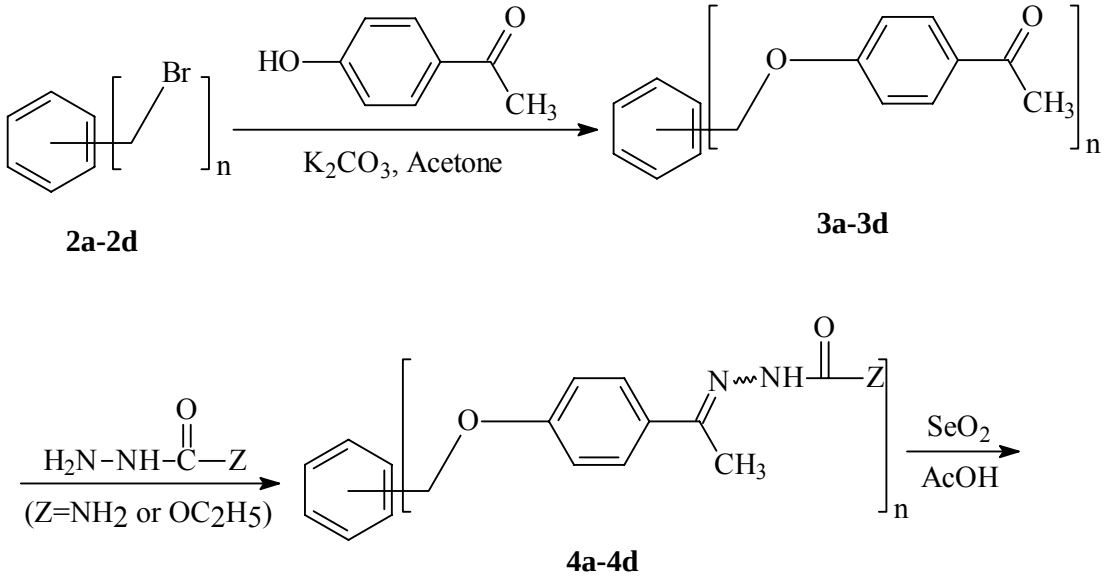
Introduction

Heterocyclic systems with multi-arm 1,2,3-thiadiazoles were recently prepared by Meier *et. al* [1-2] and heterocyclic systems containing two 1,2,3-selenadiazole rings were also recently prepared by Reddy *et. al* [3-4], but multi-arm 1,2,3-selenadiazoles are still unknown. Therefore depending on the previous experience of the principal investigator in synthesizing multi-arm 1,2,3-thiadiazoles, the analogous multi-arm selenadiazoles were prepared following the method that was first reported by Lalezari *et. al* [5-7], through reaction in the presence of acetic acid of selenium dioxide with α-ketomethylene semicarbazones or hydrazones which contain aminocarbonyl or ethoxycarbonyl groups as good leaving groups. NOE measurements showed that the (*E*)-configuration largely predominated around the CN double bond.

Selenium containing heterocycles are of increasing interest because of their interesting chemical properties [8-13] and varied biological activities [14-16]. Remarkable differences are known to exist between Se- and S-containing compounds. Due to the larger size of the Se-atom, selenium compounds show an increased polarizability and therefore they are, in general, less stable than the corresponding S-analogues [17-20]. We report herein on our efforts to generate the multi-branched benzene derivatives **1a, 1b, 1c** and **1d**, in which the 1,2,3-selenadiazole rings are linked to the central benzene core via phenoxymethylene spacers.

Scheme 1



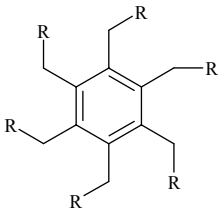
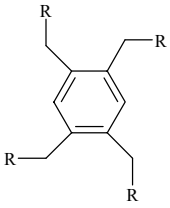
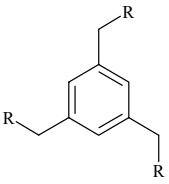
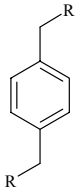
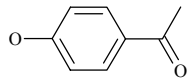
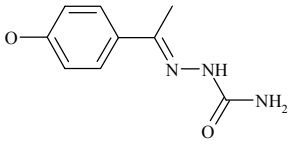
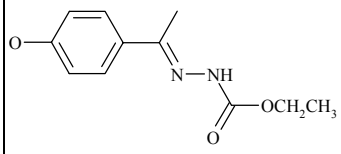
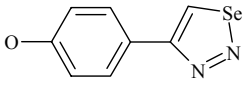
Series	n
a	6
b	4
c	3
d	2

Results and Discussion

Our synthetic procedure (see Scheme 1) started from the commercially available bromomethyl-benzene derivatives **2a-2d**. Multiple substitution with 4-hydroxyacetophenone gave the corresponding polyketones **3a-3d**, which were transformed into the target compounds **1a-1d** by the reaction of the

corresponding semicarbazones **4a-4d** or ethoxycarbonyl hydrazones **5a-5d**, essentially as described by Lalezari *et. al*. [5-7]. The yields of all three steps were optimized, so that the total overall yields for the sequences **2a** → **1a**, **2b** → **1b**, **2c** → **1c** and **2d** → **1d** amounted to 90%, 85%, 89% and 85%, respectively (Table 1).

Table 1

Ring system								
R	**Cpd.**	**Yield**	**Cpd.**	**Yield**	**Cpd.**	**Yield**	**Cpd.**	**Yield**
Br	**2a**	—	**2b**	—	**2c**	—	**2d**	—
	**3a**	87	**3b**	90	**3c**	95	**3d**	89
	**4a**	91	**4b**	81	**4c**	96	**4d**	98
	**5a**	92	**5b**	87	**5c**	85	**5d**	91
	**1a**	96	**1b**	92	**1c**	87	**1d**	60

Acknowledgements

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Experimental

General

The solvents were purified by standard procedures. The melting points (m.p.) were determined on an Electrothermal digital melting point apparatus and are uncorrected. Infrared (IR) spectra of pure substances were recorded as KBr-pellets using a Nicolet 410 FT-IR spectrometer (ν in cm^{-1}). The ^{1}H- and ^{13}C-NMR spectra were recorded on Bruker AM400 and AC200 spectrometers in $CDCl_3$ or DMSO-d_6 using TMS as internal standard. The spectral data are reported in delta (δ) units relative to

the TMS reference peak. The mass spectra were recorded using a Finnigan MAT95 field desorption (FD, 5 kV ionizing energy) instrument. The signals are given as m/z with the relative intensity between brackets. Elemental analyses were performed in the Analytical Laboratory of the Institute of Organic Chemistry of University of Mainz, Germany. Bromo compounds **2a-2d** (1,2,3,4,5,6-hexakis-, 1,2,4,5-tetrakis-, 1,3,5-tri- and 1,4-dibromomethylbenzene, respectively), ethyl hydrazine carboxylate, semicarbazide hydrochloride and sodium acetate were obtained from Aldrich.

General Procedure for the Preparation of Multi-Ketones **3a-d** [1]

A mixture of 4-hydroxyacetophenone (1 equivalent) and **2a** (0.14 equivalents), **2b** (0.21 equivalents), **2c** (0.3 equivalents) or **2d** (0.45 equivalents), potassium carbonate (1 equivalent) and potassium iodide (in the same equivalent amount as the bromo compound used) plus a few drops of Aliquat 336 were refluxed in dry acetone (100 mL) for 48 hours. The reaction was followed by TLC (eluent: chloroform) till completion. After cooling, the reaction mixture was diluted with water (50 mL) and extracted with dichloromethane (3 × 40 mL). The combined organic layers were dried over magnesium sulphate. The solvent was evaporated under vacuum and the residual solid was washed with diethyl ether. When necessary, a recrystalization from acetone or chloroform was performed.

1-{4-[2,3,4,5,6-Penta(4-acetylphenoxymethyl)benzyloxy]phenyl}-1-ethanone (**3a**).

Colorless powder (87% yield), m.p. 234-235°C; IR: ν 1675, 1604, 1508, 1239, 1002, 832 cm^{-1}; ^{1}H-NMR ($CDCl_3$): 2.50 (s, 3H, CH_3), 5.26 (s, 2H, CH_2O), 6.89, 7.83 (d, d, 2H, 2H, AA′BB′); ^{13}C-NMR ($CDCl_3$): 26.20 ($\underline{C}H_3$), 63.60 ($\underline{C}H_2O$), 137.70 (central benzene ring Cq), 114.21 and 130.70 (side chain benzene CH), 131.30, 161.80 (side chain benzene Cq), 196.40 ($\underline{C}$=O); MS: 967 (M^+, 100); Anal. % Calcd. for $C_{60}H_{54}O_{12}$: C, 74.52; H, 5.63. Found: C, 74.27; H, 5.54.

1-{4-[2,4,5-Tri(4-acetylphenoxymethyl)benzyloxy]phenyl}-1-ethanone (**3b**).

Colorless powder (90% yield); m.p. 224-226°C; IR: ν 1665, 1590, 1502, 1250, 1170, 830 cm^{-1}; ^{1}H-NMR ($CDCl_3$): 2.53 (s, 3H, CH_3), 5.23 (s, 2H, CH_2O), 6.94, 7.89 (d, d, 2H, 2H, AA′BB′), 7.65 (s, benzene ring central CH); ^{13}C-NMR ($CDCl_3$): 26.30 ($\underline{C}H_3$), 67.70 ($\underline{C}H_2O$), 129.80 (central benzene ring CH), 135.10 (central benzene ring Cq), 114.41 and 130.60 (side chain benzene CH), 131.10, 162.10 (side chain benzene Cq), 196.50 ($\underline{C}$=O); MS: 670 (M^+, 100); Anal. % Calcd. for $C_{42}H_{38}O_8$: C, 75.21; H, 5.71. Found: C, 75.13; H, 5.59.

1-{4-[3,5-Di(4-acetylphenoxymethyl)benzyloxy]phenyl}-1-ethanone (**3c**).

Pale yellow powder (100% yield); m.p. 82-83°C; IR: ν 2910, 1670, 1591, 1500, 1250, 1172, 836 cm^{-1}. ^{1}H-NMR (DMSO-d_6): 2.49 (-s, 3H, CH_3), 5.22 (s, 2H, CH_2O), 7.09, 7.90 (d, d, 2H, 2H, AA′BB′), 7.53 (s, benzene ring central CH); ^{13}C-NMR (DMSO-d_6): 26.30 ($\underline{C}H_3$), 69.20 ($\underline{C}H_2O$), 126.60 (central benzene ring CH), 137.20 (central benzene ring Cq), 114.61 and 130.50 (side chain benzene CH), 130.10, 162.00 (side chain benzene Cq), 196.30 ($\underline{C}$=O); MS: 523 (M^+, 100); Anal. % Calcd. for $C_{33}H_{30}O_6$: C, 75.84; H, 5.79. Found: C, 75.81; H, 5.68.

1-{4-[4-Mono-(4-acetylphenoxymethyl) benzyloxy] phenyl}-1-ethanone (**3d**)**.**

Colorless crystals (89% yield); m.p. 181-182°C; IR: ν 1668, 1591, 1239, 996, 823 cm^{-1}; ^{1}H-NMR ($CDCl_3$): 2.53 (s, 3H, CH_3), 5.12 (s, 2H, CH_2O), 7.00, 7.90 (d, d, 2H, 2H, AA′BB′), 7.44 (d, benzene ring central CH); ^{13}C-NMR ($CDCl_3$): 26.40 ($\underline{C}H_3$), 69.70 ($\underline{C}H_2O$), 127.80 (central benzene ring CH), 136.20 (central benzene ring Cq), 114.50 and 130.60 (side chain benzene CH), 130.60, 162.40 (side chain benzene Cq), 196.70 ($\underline{C}$=O); MS: 374 (M^+, 100); Anal. % Calcd. for $C_{24}H_{22}O_4$: C, 76.99; H, 5.92. Found: C, 76.78; H, 5.81.

General procedure for the preparation of multiple semicarbazones **4a-d**

A mixture of semicarbazide hydrochloride (1 equivalent) and sodium acetate (1 equivalent) was dissolved in absolute ethanol (40 mL). The mixture was heated for 15 min under reflux, then filtered while hot to remove precipitated sodium chloride. The filtrate was mixed with ketone **3a** (0.14 equivalents), ketone **3b** (0.21 equivalents), ketone **3c** (0.30 equivalents) or ketone **3d** (0.45 equivalents), respectively. The reaction mixture was heated to reflux then two drops of concentrated hydrochloric acid were added. The mixture was heated under reflux for overnight with continuously removal of generated water. After that the solvent was removed under vacuum and the residue was washed with diethyl ether.

1-{4-[2,3,4,5,6-Penta(4-acetylphenoxymethyl) benzyloxy]phenyl}-1-ethanone-N-aminocarbonyl semicarbazone (**4a**).

White powder (91% yield), m.p. 300°C (dec.); IR: ν 3417, 3212, 1687, 1597, 1431, 1239, 1014, 829 cm^{-1}; ^{1}H-NMR (DMSO-d_6): 2.08 (s, 3H, CH_3-C=N)), 5.37 (s, 2H, CH_2O), 6.41 (s, 2H, NH_2), 6.93, 7.70 (d, d, 2H, 2H, AA′BB′), 9.18 (s, 1H, N-H); ^{13}C-NMR (DMSO-d_6): 13.29 ($\underline{C}H_3$-C=N), 63.90 ($\underline{C}H_2O$), 137.60 (central benzene ring Cq), 114.30 and 127.50 (side chain benzene CH), 130.40, 159.60 (side chain benzene Cq), 143.90 ($\underline{C}$=N), 157.40 ($\underline{C}$=O); MS: 1309.4 (M^+, 100); Anal. % Calcd. for $C_{66}H_{72}N_{18}O_{12}$: C, 60.54; H, 5.54; N, 19.25, Found: C, 60.35; H, 5.54; N, 19.30.

1-{4-[2,4,5-Tri(4-acetylphenoxymethyl)benzyloxy]phenyl}-1-ethanone-N-aminocarbonylsemicarbazone (**4b**).

White powder (81% yield); m.p. 250°C (dec.); IR: ν 3429, 3180, 1670, 1599, 1418, 1258, 836 cm^{-1}; ^{1}H-NMR (DMSO-d_6): 2.12 (s, 3H, CH_3-C=N)), 5.34 (s, 2H, CH_2O), 5.99 (s, 2H, NH_2), 7.06, 7.86 (d, d, 2H, 2H, AA′BB′), 7.71 (s, central benzene ring CH), 9.19 (s, 1H, N-H); ^{13}C-NMR (DMSO-d_6): 13.38 ($\underline{C}H_3$-C=N), 67.08 ($\underline{C}H_2O$), 129.10 (central benzene ring CH), 134.80 (central benzene ring Cq), 114.70 and 127.50 (side chain benzene CH), 130.50, 159.70 (side chain benzene Cq), 144.00 ($\underline{C}$=N), 157.50 ($\underline{C}$=O); MS: 899 (M^+, 100); Anal. % Calcd. for $C_{46}H_{50}N_{12}O_8$: C, 62.33; H, 5.67; N, 18.17, Found: C, 62.29; H, 5.61; N, 18.05.

1-{4-[3,5-Di(4-acetylphenoxymethyl)benzyloxy]phenyl}-1-ethanone-N-aminocarbonyl semicarbazone (**4c**).

Pale yellow powder (100% yield); m.p. 240°C (dec.); IR: ν 3417, 3250, 1681, 1579, 1508, 1470, 1226, 829 cm^{-1}; ^{1}H-NMR (DMSO-d_6): 2.13 (s, 3H, CH_3-C=N)), 5.15 (s, 2H, CH_2O), 6.55 (s, 2H, NH_2), 6.98, 7.76 (d, d, 2H, 2H, AA′BB′), 7.49 (s, central benzene ring CH), 9.25 (s, 1H, N-H); ^{13}C-NMR (DMSO-d_6): 13.38 ($\underline{C}H_3$-C=N), 69.15 ($\underline{C}H_2O$), 126.44 (central benzene ring CH), 137.76 (central benzene ring Cq), 114.54 and 127.50 (side chain benzene CH), 131.20, 158.73 (side chain benzene Cq), 144.11 ($\underline{C}$=N), 157.90 ($\underline{C}$=O); MS: 693.77 (M^+, 100); Anal. % Calcd. for $C_{36}H_{39}N_9O_6$: C, 61.46; H, 5.61; N, 18.70, Found: C, 63.32; H, 5.51; N, 18.63.

1-{4-[4-(4-acetylphenoxymethyl)benzyloxy]phenyl}-1-ethanone-N-aminocarbonyl semicarbazone (**4d**).

White powder (100% yield); m.p. 300°C (dec.); IR: ν 3417, 3212, 1681, 1604, 1502, 1418, 1239, 1014, 829 cm^{-1}; ^{1}H-NMR (DMSO-d_6): 2.12 (s, 3H, CH_3-C=N)), 5.20 (s, 2H, CH_2O), 5.90 (s, 2H, NH_2), 7.08, 7.89 (d, d, 2H, 2H, AA′BB′), 7.45 (d, central benzene ring CH), 9.21 (s, 1H, N-H); ^{13}C-NMR (DMSO-d_6): 13.30 ($\underline{C}H_3$-C=N), 69.30 ($\underline{C}H_2O$), 127.80 (central benzene ring CH), 136.41 (central benzene ring Cq), 114.50 and 128.00 (side chain benzene CH), 131.17, 159.70 (side chain benzene Cq), 143.00 ($\underline{C}$=N), 158.70 ($\underline{C}$=O); MS: 488.5 (M^+, 100); Anal. % Calcd. for $C_{26}H_{28}N_6O_4$: C, 63.92; H, 5.78; N, 17.20, Found: C, 63.71; H, 5.72; N, 17.15.

General procedure for the preparation of multiple hydrazones **5a-d** [1].

A solution of di- or tri- or tetra- or hexaketone **3a-d** (1 equivalent), a few drops of concentrated hydrochloric acid and 6, 9, 12 or 18 equivalents of ethyl hydrazinecarboxylate in dry chloroform (50 mL) was heated under reflux overnight with continuously removal of generated water. The solution was concentrated and the residue was washed with diethyl ether and chloroform.

1-{4-[2,3,4,5,6-Penta(4-acetylphenoxymethyl)benzyloxy]phenyl}-1-ethanone-N-ethoxycarbonyl hydrazone (**5a**).

White solid powder (92% yield); m.p. 293°C (dec.); IR: ν 3231, 1719, 1610, 1502, 1233, 1047, 829 cm^{-1}; ^{1}H-NMR (DMSO-d_6): 1.23 (t, 3H, $\underline{C}H_3CH_2$), 2.12 (s, 3H, CH_3-C=N)), 4.13 (q, 2H, $CH_3\underline{C}H_2$), 5.29 (s, 2H, CH_2O), 6.95, 7.58 (d, d, 2H, 2H, AA′BB′), 9.96 (s, 1H, N-H); ^{13}C-NMR (DMSO-d_6): 14.23 ($\underline{C}H_3CH_2$), 15.01 ($\underline{C}H_3$-C=N), 60.95 ($CH_3\underline{C}H_2O$), 64.36 ($\underline{C}H_2O$-ph), 138.09 (central benzene ring Cq), 114.86 and 127.94 (side chain benzene CH), 131.93, 159.41 (side chain benzene Cq), 149.25 ($\underline{C}$=N), 154.76 ($\underline{C}O_2$); MS: 1484 (M^+,100); Anal. % Calcd. for $C_{78}H_{90}N_{12}O_{18}$: C, 63.15; H, 6.11; N, 11.33, Found: C, 62.79; H, 6.27; N, 11.44.

1-{4-[2,4,5-Tri-(4-acetylphenoxymethyl)benzyloxy]phenyl}-1-ethanone-N-ethoxycarbonyl hydrazone (**5b**).

White powder (87% yield), m.p. 211-213°C; IR: ν 3200, 3045, 1700, 1596, 1492, 1235, 1040, 828 cm^{-1}; ^{1}H-NMR (DMSO-d_6): 1.24 (t, 3H, $\underline{C}H_3CH_2$), 2.16 (s, 3H, CH_3-C=N)), 4.16 (q, 2H, $CH_3\underline{C}H_2$), 5.27 (s, 2H, CH_2O), 7.03, 7.65 (d, d, 2H, 2H, AA′BB′), 7.71 (s, central benzene ring CH), 9.98 (s, 1H, N-H); ^{13}C-NMR (DMSO-d_6): 14.28 ($\underline{C}H_3CH_2$), 15.19 ($\underline{C}H_3$-C=N), 60.98 ($CH_3\underline{C}H_2O$), 67.40 ($\underline{C}H_2O$-ph), 129.37 (central benzene ring CH), 135.43 (central benzene ring Cq), 115.08 and 128.00 (side chain benzene CH), 131.76, 159.33 (side chain benzene Cq), 148.70 ($\underline{C}$=N), 154.80 ($\underline{C}O_2$); MS: 1015 (M^+, 100); Anal. % Calcd. for $C_{54}H_{62}N_8O_{12}$: C, 63.89; H, 6.16; N, 11.04, Found: C, 63.58; H, 6.09; N, 10.97.

1-{4-[3,5-Di(4-acetylphenoxymethyl)benzyloxy]phenyl}-1-ethanone-N-ethoxycarbonyl hydrazone (**5c**).

Pale yellow powder (85% yield), m.p. 202-204°C; IR: ν 3200, 3035, 1705, 1600, 1503, 1238, 1040, 830 cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 1.24 (t, 3H, $\underline{C}H_3CH_2$), 2.17 (s, 3H, CH_3-C=N)), 4.15 (q, 2H, $CH_3\underline{C}H_2$), 5.18 (s, 2H, CH_2O), 7.03, 7.67 (d, d, 2H, 2H, AA′BB′), 7.52 (s, central benzene ring CH), 9.99 (s, 1H, N-H); ^{13}C-NMR (DMSO-d_6): δ 14.30 ($\underline{C}H_3CH_2$), 15.20 ($\underline{C}H_3$-C=N), 60.90 ($CH_3\underline{C}H_2O$), 69.60 ($\underline{C}H_2O$-ph), 126.90 (central benzene ring CH), 138.06 (central benzene ring Cq), 115.10 and 128.00 (side chain benzene CH), 131.60, 159.50 (side chain benzene Cq), 148.70 ($\underline{C}$=N), 154.20 ($\underline{C}O_2$); MS: 781 (M^+, 100); Anal. % Calcd. for $C_{42}H_{48}N_6O_9$: C, 64.60; H, 6.20; N, 10.76, Found: C, 64.48; H, 6.13; N, 10.50.

1-{4-[4-Mono(4-acetylphenoxymethyl)benzyloxy]phenyl}-1-ethanone-N-ethoxycarbonyl hydrazone (**5d**).

White powder (91% yield); m.p. 259-260°C; IR: ν 3205, 3035, 1705, 1600, 1500, 1230, 822 cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 1.22 (t, 3H, $\underline{C}H_3CH_2$), 2.15 (s, 3H, CH_3-C=N)), 4.16 (q, 2H, $CH_3\underline{C}H_2$), 5.10 (s, 2H, CH_2O), 6.99, 7.87 (d, d, 2H, 2H, AA′BB′), 7.43 (d, central benzene ring CH), 9.99 (s, 1H, N-H); ^{13}C-NMR (DMSO-d_6): δ 13.60 ($\underline{C}H_3CH_2$), 14.70 ($\underline{C}H_3$-C=N), 60.80 ($CH_3\underline{C}H_2O$), 67.80 ($\underline{C}H_2O$-Ph), 127.60 (central benzene ring CH), 136.30 (central benzene ring Cq), 114.50 and 127.60 (side chain benzene CH), 130.50, 160.10 (side chain benzene Cq), 148.81 ($\underline{C}$=N), 154.30 ($\underline{C}O_2$); MS: 547 (M^+, 100); Anal. % Calcd. for $C_{30}H_{34}N_4O_6$: C, 65.92; H, 6.27; N, 10.25, Found: C, 65.99; H, 6.18; N, 10.15.

General procedure for preparation of multiple 1,2,3-selenadiazoles **1a-d**

Hydrazone **5a** (0.47 mmol) or **5b** (0.59 mmol) or **5c** (0.9 mmol) or **5d** (0.27 mmol) was dissolved in glacial acetic acid (30 mL) with vigorous stirring and gentle heating to 40-45°C. The solution was treated with selenium dioxide powder (8.46 mmol, 7.08 mmol, 8.1 mmol or 0.81 mmol, respectively) and the mixture was kept under gentle heating with vigorous stirring. After 2 min, the color of the mixture becomes red. Monitoring of the reaction by TLC showed that the reaction was complete in two days. The mixture was filtered and the filtrate was poured into ice water and extracted with chloroform (3 × 50 mL). The combined organic layers were washed with saturated sodium hydrogen

carbonate solution and dried using magnesium sulphate. The solvent was removed under vacuum. The crude product was purified by chromatography using methanol or ethyl acetate as eluents, followed by recrystallization from chloroform/hexane.

4-(4-{2,3,4,5,6-Penta[4-(1,2,3-selenadiazole-4-yl)phenoxymethyl]benzyloxy}phenyl)-1,2,3-selenadiazole (**1a**).

Yellow-orange solid (100%); m.p. 77-78°C; IR: ν 3096, 2975, 1739, 1611, 1527, 1469, 1220, 989, 841 cm^{-1}; ^{1}H-NMR ($CDCl_3$): 5.27 (s, 2H, CH_2O), 7.06, 7.17 (d, d, 2H, 2H, AA′BB′), 9.68 (s, 1H, CHSe); ^{13}C-NMR ($CDCl_3$): 63.62 ($\underline{C}H_2O$), 128.50 (central benzene ring Cq), 115.36 and 130.20 (side chain benzene CH), 119.20, 152.40 (side chain benzene Cq), 159.61 ($\underline{C}$=N), 137.70 ($\underline{C}$HSe); MS: 1500 (M^+, 100); Anal. % Calcd. For $C_{60}H_{42}N_{12}O_6Se_6$: C, 48.01; H, 2.82; N, 11.20; Se, 31.57, Found: C, 47.91; H, 2.74; N, 11.11.

4-(4-{2,4,5-Tri[4-(1,2,3-selenadiazole-4-yl)phenoxymethyl]benzyloxy}phenyl)-1,2,3-selenadiazole (**1b**).

Yellow-orange solid (92% yield); m.p. 87-88°C; IR: ν 3096, 2930, 1725, 1611, 1527, 1469, 1245, 1040, 822 cm^{-1}; ^{1}H-NMR (CDCl3): 5.25 (s, 2H, CH_2O), 7.12, 7.22 (d, d, 2H, 2H, AA′BB′), 7.70 (s, benzene central ring CH), 9.71 (s, 1H, CHSe); ^{13}C-NMR ($CDCl_3$): 67.70 ($\underline{C}H_2O$), 124.00 (central benzene ring CH), 129.80 (central benzene ring Cq), 115.89 and 130.12 (side chain benzene CH), 118.80, 152.60 (side chain benzene Cq), 159.92 ($\underline{C}$=N), 136.40 ($\underline{C}$HSe); MS: 1026 (M^+, 100); Anal. % Calcd. For $C_{42}H_{30}N_8O_4Se_4$: C, 49.13; H, 2.95; N, 10.91; Se, 30.77, Found: C, 49.10; H, 2.75; N, 10.71.

4-(4-{3,5-Di[4-(1,2,3-selenadiazole-4-yl)phenoxymethyl]benzyloxy} phenyl)-1,2,3-selenadiazole (**1c**).

Yellow-orange solid (87% yield); m.p.100-102°C; IR: ν 3096, 2917, 1738, 1610, 1534, 1450, 1239, 1046, 835 cm^{-1}; ^{1}H-NMR ($CDCl_3$): 5.15 (s, 2H, CH_2O), 7.11, 7.20 (d, d, 2H, 2H, AA′BB′), 7.49 (s, central benzene ring CH), 9.72 (s, 1H, CHSe); ^{13}C-NMR ($CDCl_3$): 69.69 ($\underline{C}H_2O$), 126.00 (central benzene ring CH), 129.70 (central benzene ring Cq), 115.99 and 130.03 (side chain benzene CH), 118.80, 149.15 (side chain benzene Cq), 160.15 ($\underline{C}$=N), 137.60 ($\underline{C}$HSe); MS: 789 (M^+, 100); Anal. % Calcd. For $C_{33}H_{24}N_6O_3Se_3$: C, 50.20; H, 3.06; N, 10.64; Se, 30.01, Found: C, 50.10; H, 3.00; N, 10.59.

1,4-Bis[4-(1,2,3-selenadiazol-4-yl)phenoxymethyl]benzene (**1d**).

Yellow-orange solid (60% yield); m.p. 160-162°C; IR: ν 3077, 2911, 1732, 1610, 1533, 1456, 1239, 1008, 822 cm^{-1}; ^{1}H-NMR (DMSO-d_6): 5.15 (s, 2H, CH_2O), 7.12, 7.21 (d, d, 2H, 2H, AA′BB′), 7.47 (d, benzene central ring CH), 9.72 (s, 1H, CHSe); ^{13}C-NMR (DMSO-d_6): 70.00 ($\underline{C}H_2O$), 127.89 (central benzene ring CH), 129.18 (central benzene ring Cq), 116.10 and 130.00 (side chain benzene CH), 121.00, 152.00 (side chain benzene Cq), 160.00 ($\underline{C}$=N), 138.00 ($\underline{C}$HSe); MS: 552 (M^+, 100); Anal. % Calcd. For $C_{24}H_{18}N_4O_2Se_2$: C, 52.18; H, 3.28; N, 10.14; Se, 28.60, Found: C, 52.03; H, 3.25; N, 10.20.

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